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quantities of peroxides (principally H_2O_2) and aldehydes ($HCHO$ and CH_3CHO) reach, with a maximum total increment of pressure amounting to $\Delta p = 30$ mm, certain maximum values (1.8 : 11.5 and 4.5 mm, respectively), after which the concentration of peroxides begins to decrease (to 0.2 mm towards the end of the interaction), while the concentration of aldehydes remains constant. Semilogarithmic anamorphosis of the concentration curves of the peroxides and aldehydes gives straight lines to the points where these intermediate products reach maximum concentrations. This proves that accumulation takes place according to an exponential law. As far as alcohols are concerned, only methyl alcohol is obtained in the oxidation of propane. Its quantity increases throughout the entire run of the reaction, reaching at the end a value of 25 mm.

Propylene and ethylene accumulate during the entire run of the oxidation, reaching at its end 19 and 8 mm, respectively. Throughout the extent of the entire reaction the relationship $C_3H_6 : C_2H_4 \approx 2.3$. Methane is found in the products of the reaction in quantities of the same order as the quantity of ethylene.

A fact worth noting is that the ratio of the amount of propane used for the formation of oxygen-containing products -- CH_3OH , $HCHO$, CH_3CHO , oxygen, CO , CO_2 , to its amount used for the formation of C_3H_6 , C_2H_4 and CH_4 , increases during the run of the reaction (from 0.6 at $p = 10$ mm to 1.47 at $p = 60$ mm). This fact must be considered in drawing up the scheme of the process.

A full balance on C_3H_8 and O_2 for the entire run of the reaction is set forth in Table 1, from which it follows that the analysis covers all the main products of the oxidation. The ratio of formal water, determined by calculation from the balance, to the total amount of $CO + CO_2$ remains constant during the run of the reaction and is nearly equal to 1.4.

Calculation of the reaction rate from the increment in total pressure and consumption of O_2 shows that the maximum rate of consumption of O_2 occurs at the moment ($\Delta p = 30$ mm) when the quantities of peroxide and aldehydes reach their maximum, while the maximum rate of increase in total pressure takes place much earlier ($p = 17$ mm). In this is found one of the kinetic manifestations of the difference between the processes of oxidation of C_3H_8 and C_3H_6 [1].

The influence of adding CH_3CHO , C_3H_6 and CH_3OH on the oxidation of the mixture $C_3H_8 + O_2$ at $T = 350^\circ$ and $P_{initial} = 282$ mm was studied. This proved that adding 1.9 mm CH_3CHO (i.e., two and one half times less than its maximum accumulation in the reaction) shortens the time required for reaching the maximum rate by a factor of 8 and doubles the absolute value of the latter. The quantities of $HCHO$ and CH_3CHO found at the end of the reaction (even when adding eight mm CH_3CHO to the initial mixture) remain the same as they would without any addition of CH_3CHO . Adding C_3H_6 and CH_3OH to the original mixture effected an increase in final yield of these substances equal approximately to the amount added. From this it follows that C_3H_6 and CH_3OH formed during the oxidation are not subject to further oxidation under our conditions.

In experiments on prepared mixtures analogous to those which were described for the oxidation of C_3H_8 (2), it was found that in the case of C_3H_8 , the substance which determines the branched-degenerate character of the oxidation is also CH_3CHO .

The course of the oxidation of propane was determined by considering the following:

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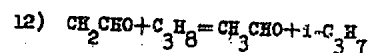
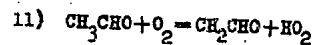
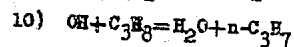
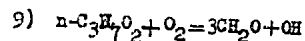
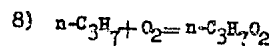
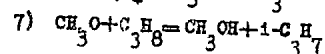
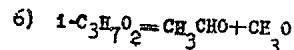
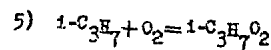
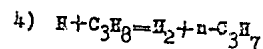
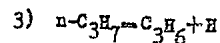
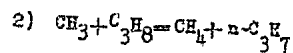
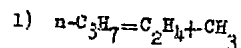
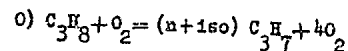
a) The oxidation of propane does not take place through the oxidation of C_3H_6 formed in the course of the reaction. This is indicated by the result of experiments in which C_3H_6 was added to the initial mixture (see above).

b) C_3H_6 , C_2H_4 , CH_4 and H_2 , the usual products of propane cracking, are also obtained by cracking in its oxidation. The fact that in the case of oxidation these products are formed at somewhat lower temperatures, is explained by the presence of O_2 , which noticeably facilitates the course of the reaction along the path of cracking.

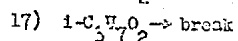
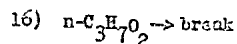
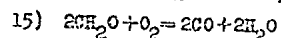
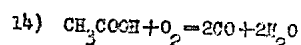
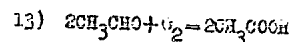
c) $HCHO$, formed in the reaction, is not a product of the degradation of CH_3CHO . This follows from the absence of any influence of addition of CH_3CHO to the initial mixture on the amount of $HCHO$ found at the end of the reaction (see above).

d) Further oxidation of the aldehydes formed in the reaction proceeds according to the summary equations: $HCHO + \frac{1}{2} O_2 = CO + H_2O$ and $CH_3CHO + \frac{1}{2} O_2 = 2CO + 2H_2O$. By the same course of oxidation of aldehydes, CO_2 is obtained and, just like CO_2 is obtained in equimolecular quantities with the water formed at the same time.

e) Water is formed not only in the oxidation of aldehydes. This follows from the fact that the relationship of $H_2O:(CO+CO_2) > 1 (\approx 1.4$ throughout the entire run of the reaction).



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The scheme postulates two directions of the reaction, cracking and oxidation. The first is brought about by the decomposition of $\text{n-C}_3\text{H}_7$ only, the second by the oxidation of $\text{n-C}_3\text{H}_7$ as well as $\text{i-C}_3\text{H}_7$. In this connection it is assumed that the free radicals and atoms arising from the decomposition and oxidation of $\text{n-C}_3\text{H}_7$ (i.e., CH_3 , H , OH) are sufficiently active for regeneration of $\text{n-C}_3\text{H}_7$ during the reaction starting with the initial propane, while the radicals formed by way of oxidation of $\text{i-C}_3\text{H}_7$ and in the course of oxidation of CH_3CHO leading to branching (i.e., to CH_2O and CH_2CHO), by virtue of their weaker activities are capable of regenerating $\text{i-C}_3\text{H}_7$ only [in the reaction starting with propane]. In this manner, the branched part of the oxidation path of the reaction turns out to be fully separated from the cracking. This makes it possible to explain the observed growth, during the course of the process, of the ratio of C_3H_8 used up in the oxidation, to C_3H_8 used up in cracking (see above).

Out of the scheme and the assumed conditions the following relations follow:

1. The amounts of actually formed (i.e., without taking into consideration further oxidation) CH_3OH and CH_3CHO must be equal to each other.
2. The amount of H_2O obtained other than by oxidation of aldehydes, i.e., $[\text{H}_2\text{O} - (\text{CO} + \text{CO}_2)]$ must equal one third of the actually formed HCHO .
3. Lowering of the concentration of O_2 during the course of the reaction must be reflected in an increase of the ratio of actually formed CH_3CHO to HCHO .

In checking these relationships, it is necessary to calculate the amount of actually formed HCHO and CH_3CHO at every given moment of the reaction. This can be done in the following way. Since the formed CH_3OH does not undergo further oxidation, its analytically determined amount is equal to the amount of actually formed CH_3CHO [prior to the latter's conversion]. The difference between the CH_3CHO determined in this manner and the analytically determined CH_3CHO gives the amount of CH_3CHO subjected to oxidation. Subtracting from the analytically found sum of $(\text{CO} + \text{CO}_2)$ twice the amount of oxidized CH_3CHO , we get the amount of $(\text{CO} + \text{CO}_2)$ formed through the oxidation of HCHO . Adding it to the analytically determined amount of HCHO , we find the amount of actually formed HCHO .

Calculating in this manner the amounts of CH_3CHO and HCHO actually formed in the course of the reaction, one may compare one third of the virtually formed HCHO with the experimentally obtained difference $[\text{H}_2\text{O} - (\text{CO} + \text{CO}_2)]$ and compute the ratio of CH_3CHO to HCHO . As seen by the values in Table II, this gives a good confirmation of the relationships derived from the proposed scheme.

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 2. V. Shtern and S. Polyak, DAN SSSR, Vol 66, 235, (1949).

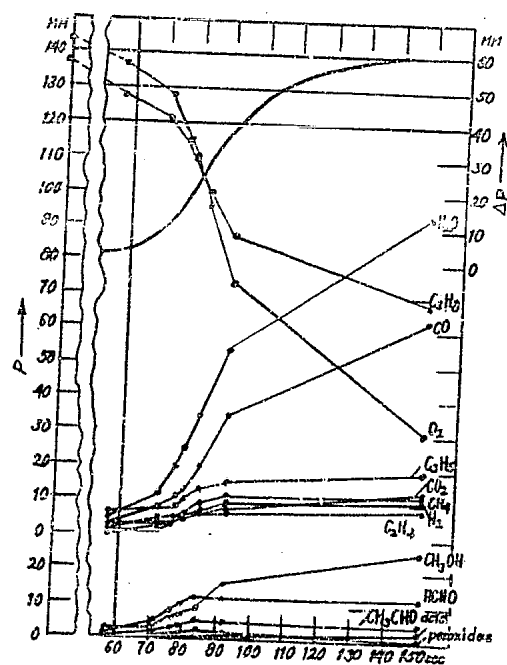


Fig. 1. Oxidation in Propane-Oxygen Mixture.

Table 1

Mixture of $C_3H_8 + O_2$; $T=350^\circ$; $P_{initial}=232$ mm Hg

Pressure Increment (mm)	Time Mixture in Vessel (sec)	C_3H_8		H_2		Difference	O_2		Difference	H_2O by Residual H_2 and C_2
		Expanded	Found	Expanded	Found		Expanded	Found		
3	57	30	31.4	40	34.2	5.8				
10	71.5	51	51.5	68	52	16	6.7	4.45	2.25	4.5
17	76.5	72	70.2	96	71.8	24.2	16	10	6	12
22	79.2	87	84.6	116	90.6	25.4	29	19.2	9.8	20
30	84	117	115.4	160	114	46	34	21.8	12.2	24.4
40	92.5	153	156	204	148.5	55.5	48.3	31	17.3	34.6
60	150	210	208.2	280	180.5	99.5	70.6	43.5	27.1	54.2
							114	67	47	93

Table 2

Mixture $C_3H_8 + O_2$; $T=350^\circ$; $P_{initial}=280$ mm Hg

Pressure increment (mm)	10	17	22	30	40	60
One third of actually formed of $HCHO$ in mm (calculated)	3.56	5.55	6.9	9.7	10.6	15.8
$H_2O - (CO + CO_2)$ in mm (from experiment)	3.4	5.2	6.9	8.9	11.3	16.7
Ratio of actually formed CH_3CHO : $HCHO$	0.215	0.33	0.32	0.30	0.49	0.54

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